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Project Summary

Evaluating the Relation Between Ozone, NO_x and Hydrocarbons: The Method of Photochemical Indicators

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The method of photochemical indicators is a way to evaluate the sensitivity of O_3 to its two main precursors, nitrogen oxides (NO_x) and reactive organic gases (ROG), directly from ambient measurements. The method is based on identifying measureable species or species ratios that are closely associated with O_3-NO_x-ROG predictions in photochemical models. Several species of this type have been identified: O_3/NO_y (where NO_y is total reactive nitrogen), O_3/NO_z (where NO_z=NO_y-NO_x, O_3/HNO_3, H_2O_2/HNO_3, $H_2O_2/N0_z$, and H_2O_2/NO_y' In each case, high values of the proposed indicator are associated with NO_x-sensitive chemistry in models and low values are associated with ROG-sensitive chemistry. This report presents a summary of O_3-NO_x-ROG sensitivity in models and the chemistry that motivate the choice of species as photochemical indicators. It shows the correlation between model NO_x-ROG predictions and indicator values for a variety of models, including simulations for Lake Michigan, the northeast corridor, Atlanta and Los Angeles. The indicator NO_x-ROG correlation remains consistent in model scenarios with radically different assumptions about anthropogenic and biogenic emission rates and meteorology and in models with different chemical mechanisms. The report shows correlations between O_3, NO_z and H_2O_2 in models and in ambient measurements, which provide a basis for evaluating the accuracy of critical assumptions associated with the indicator method. Case studies are described for Atlanta and Los Angeles in which measured values of indicator ratios were used as a basis for evaluating model scenarios. It is shown in which model scenarios with different NO_x-ROG predictions often give similar values for peak O_3 but different values for indicator ratios. The case studies illustrate how comparisons between model results and measured indicator values can be used as a basis for model evaluation. Uncertainties associated with the indicator method (including measurement uncertainties, dry deposition and surface effects) are discussed.

This Project Summary was developed by EPA's National Exposure Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

For many years there has been uncertainty about the relation between low-level ozone and its two major anthropogenic precursors: reactive organic gases (ROG) and nitrogen oxides (NO_x). It is generally known that for some conditions ozone concentrations increase with increasing NO_x emissions and are largely independent of ROG, while for other conditions ozone increases with ROG and does not increase (or may even decrease) with NO_x. However, it is difficult to determine whether individual air pollution events are dominated by NO_x-sensitive or ROG-sensitive chemistry.

The uncertain relationship between ozone, ROG and NO_x has made it especially difficult to develop effective control policies for ozone. Because of the complex relationship between ozone and its precursors, there is far greater uncertainty about the effectiveness of control strategies for ozone than for other pollutants associated with air quality violations. A control strategy that relies on reductions in emissions of ROG will not be effective in a region where ozone concentrations are driven by NO_x-sensitive chemistry. Similarly, a control strategy that relies on NO_x reductions will not be effective during air pollution events with ROG-sensitive chemistry.

The task of analyzing the ozone-NO_x-ROG relationship is commonly based on predictions from photochemical models. These models use estimates for emission rates of ozone precursors in combination with meteorological information (wind speeds, vertical diffusion, temperatures, etc.) and a representation of ozone chemistry in order to simulate the ozone formation process for a specific air pollution event. Predictions for the effectiveness of ROG vs. NO_x controls are derived by repeating the simulations with reduced emission rates for ROG or NO_x. The accuracy of these control strategy predictions has frequently been called into question, largely because of uncertainties associated with emission inventories. These uncertainties have a large impact on model predictions of the effectiveness of ROG vs. NO_x controls. It is possible to generate model scenarios with either NO_x- and ROG-sensitive chemistry while remaining within the bounds of uncertainty associated with emissions and other model inputs.

A more fundamental problem with the model-based approach for O_3-NO_x-ROG sensitivity is the difficulty in evaluating model predictions against real-world measurements. There is no direct way to evaluate a control strategy prediction, because it is never possible to repeat an air pollution event with reduced ROG or NO_x emissions and compare its outcome with model results. Model evaluations can only be done by comparing predictions from the model base case with ambient measurements. The problem with most model evaluations is that the accuracy of model predictions for the base case does not guarantee that model predictions for control strategies are also accurate. In particular, the most common test of model performance – comparison with ambient ozone – gives no basis for confidence in model predictions for control strategies. This is because different model scenarios often give similar values for ozone in the base case, while giving very different predictions for the response of ozone to reductions in ROG or NO_x.

This report presents a new approach to the problem of evaluating O_3-NO_x-ROG sensitivity: the *method of photochemical indicators.* The goal of the method is to identify measureable species or species ratios that are closely linked to model control strategy predictions, so that NO_x-sensitive or ROG-sensitive chemistry can be associated with specific values of these species ratios. If successful, the method of photochemical indicators would provide a way to evaluate NO_x-ROG sensitivity based solely on ambient measurements, without using models. A more modest application of the method would be to evaluate the performance of model scenarios. The nature of the indicator ratios associated with this method is that they will always assume different values in models with NO_x-sensitive chemistry as opposed to models with ROG-sensitive chemistry. Thus, the indicator ratios (unlike ozone) provide a basis for choosing between NOx sensitive and ROG-sensitive model scenarios.

The method of photochemical indicators is part of a broader attempt to develop observation-based methods (OBMs) that seek to analyze O_3-NO_x-ROG chemistry based on extensive field measurements rather than model predictions.

The method of photochemical indicators was developed based on a series of photochemical model applications designed to represent a wide range of physical conditions and situations. These have included simulations for four metropolitan regions: the Lake Michigan airshed, the New York–Boston urban corridor, Atlanta, and Los Angeles. They have included simulations with anthropogenic ROG emissions doubled from inventory estimates. They have included scenarios with anthropogenic ROG emissions reduced by half from inventory estimates, reflecting conditions that may occur in Europe today or in the U.S. following the application of an effective ROG control program. They have included scenarios with biogenic ROG emissions based on the current BEIS2 inventory and also on the older BEIS1 inventory with much lower emission rates and scenarios with zero biogenic emissions. They have included simulations with changed wind speeds and vertical mixing rates in order to represent conditions that might be either more or less stagnant than the events used as test cases. They have included results from two very different model types: a regional-scale model developed by Sillman et al. at the University of Michigan and the Urban Airshed Model (UAM-IV), familiar to air pollution researchers. These two models include different representations of photochemistry: a mechanism based on Lurmann et al. (similar to the more familiar SAPRC mechanism) with various updates and isoprene chemistry based on work by Paulson and Seinfeld in the Michigan model; and the Carbon Bond IV mechanism in UAM-IV.

Species and species ratios that can be used as indicators for NO_x-ROG sensitivity were sought based on an analysis of model results. In order to be useful as a photochemical indicator a species or species ratio must satisfy the following four criteria:

(i) The indicator must involve measureable species.

(ii) The indicator must consistently show different values in model scenarios with NO_x-sensitive chemistry as opposed to model scenarios with ROG-sensitive chemistry. The difference between NO_x-sensitive and ROG-sensitive indicator values must also be large enough so that the NO_x-ROG indication is less likely to be obscured by uncertainties in measurement techniques.

(iii) The correlation between indicator values and NO_x-ROG sensitivity must remain reasonably constant in models with widely different assumptions. The purpose of the method would be undermined if the indicator correlation were limited to models with a fixed range of assumptions, e.g. about biogenic ROG.

(iv) The indicator should be closely linked with the chemical factors that govern NO_x-ROG sensitivity. It should not just represent an empirical curve-fitting exercise or be an artifact of an individual model.

Two classes of species have been identified that appear to meet these criteria. These species are as follows.

Ratios involving ozone and total reactive nitrogen: (O_3/NO_y), where NO_y represents total reactive nitrogen (NO_x PAN, HNO_3, alkyl nitrates and other nitrogen-containing species produced from NO_x; (O_3/NO_z), where NO_z represents NO_x reaction products, NO_y-NO_x; and (O3/HNO3).

Ratios involving hydrogen peroxide and total reactive nitrogen: (H_2O_2/HNO_3), (H_2O_2/NO_z), and (H_2O_2/NO_y).

In each case, a high value for the indicator ratio corresponds to a situation in

which the ozone concentration is primarily sensitive to NO_x, while a low value corresponds to a situation in which O_3 is primarily sensitive to ROG. This interpretation applies only for indicator values during the afternoon (concurrent with peak O_3) and only for NO_x-ROG sensitivity at the same location as the indicator value.

Among these alternatives, the ratios involving hydrogen peroxide, especially (H_2O_2/HNO_3), provide more consistent results in photochemical models and are more closely linked to the photochemical processes that drive NO_x-ROG chemistry, but these are also more difficult to measure. Among the ratios involving ozone, (O_3/NO_z) has a stronger link with NO_x-ROG chemistry than (O_3/NO_y), but the latter has certain advantages associated with situations involving power plants.

An important component of the indicator method concerns the need to evaluate the accuracy of the indicator predictions. The correlation between NO_x-ROG sensitivity and the indicator ratios is based entirely on the results of photochemical models. As such, the indicator method faces the same type of challenge as the conventional photochemical models: how can the predicted NO_x-ROG sensitivity be proven?

Model results have suggested an important test for the validity of the method. The chemistry associated with NO_x-ROG sensitivity and the indicator ratios also suggests that a linear correlation should be found between O_3 and the sum: $NO_z+2H_2O_2$, evaluated during the afternoon following a period of photochemical activity. This linear correlation is predicted in three-dimensional models that include both chemistry and transport, and is presented. The correlation is closely associated with the role of O_3, NO_z and H_2O_2 as indicators for NO_x-ROG sensitivity. It is well-known that O_3 increases with NO_z but that the rate of increase (dO_3/dNO_z) decreases at higher NO_z and is lower in some urban areas (e.g. Los Angeles) relative to rural sites. The indicator method provides an additional interpretation: high O_3/NO_z ratios in rural areas represent NO_x-sensitive chemistry while low O_3/NO_z ratios in central Los Angeles represent ROG-sensitive chemistry. If this interpretation is valid, then the correlation between O_3 and the sum $NO_z+2H_2O_2$ will remain linear, even while the O_3-NO_z slope varies. Thus, an examination of measured O_3, NO_z and H_2O_2 provides both a general evaluation of the indicator method and a test for problems (e.g. measurement errors or erroneous model assumptions) in each individual application of the method.

In summary, the indicator method provides several advantages over conventional methods of analysis of O_3-NO_x-ROG sensitivity. Unlike conventional photochemical models, the indicator predictions are not sensitive to assumptions about emission rates for anthropogenic or biogenic ROG. When used in combination with photochemical models the indicator method provides a meaningful evaluation of the accuracy of model NO_x- ROG predictions. Finally, the indicator method includes a diagnostic test for its own accuracy, based on the predicted linear correlation between O_3, NO_z and H_2O_2. The indicator method can be applied based on measurements for just three species, O3, NO_x and NO_y, although the inclusion of measurements of H_2O_2, HNO_3 and CO would improve the reliability of the method.

The indicator method, like any new approach, involves problems and uncertainties that are not present in other methods. A list of caveats in the report is provided for researchers who seek to use the indicator method.

The report presents a summary of research on the indicator method to date. Section 2 provides background information on the chemistry of O_3, NO_x and ROG that serves as a motivating factor for the selection of the various indicator ratios. This section also presents a concise summary of the current understanding of O_3-NO_x-ROG sensitivity that has emerged in recent years. The state of science associated with O_3-NO_x-R0G chemistry has seen great changes in the past ten years. The summary in Section 2 may serve both as an introduction to the field and a review for experienced researchers and regulators.

Section 3 of the report presents the correlation between O_3-NO_x-ROG predictions and the various indicator ratios in photochemical models. It includes a description of the models used, general results for O_3-NO_x-ROG sensitivity, the extent of variation of the indicator NO_x-ROG correlation in different model scenarios, and methods for quantitatively identifying the indicator values corresponding to the transition between NO_x- and ROG-sensitive chemistry. It also shows results for alternative choices (NO_y, AIRTRAK, O3/NOx, ROG/NO_x) which do not perform as well as the recommended indicator ratios. A complete presentation of model results is also included in the Appendix.

Section 4 examines the correlation between O_3, NO_z and H_2O_2 as predicted by photochemical models and as observed during field measurement campaigns. As described above, this correlation represents a critical test for the accuracy of the indicator method.

Section 5 shows results from applications of the indicator method for specific events in Atlanta and Los Angeles. These results include comparisons between predicted indicator values from a series of model scenarios, each designed to give different predictions for NO_x-ROG chemistry. These predictions are compared with measured indicator species and ratios, which are used as a basis for accepting the results of some model scenarios and rejecting others. The comparison between model and measured values of photochemical indicators associated with predicted and observed (non-paired) peak O_3 is proposed as a criterion for evaluating model performance. This criterion provides a much stronger basis for model evaluation then criteria based solely on model vs. measured O_3. It is hoped that these case studies can be used as examples for future applications.

Chemistry of O_3, NO_x and ROG

The original understanding that NO_x-ROG sensitivity is determined by ROG/NO_x ratios has been greatly modified in recent years. Additional factors include the impact of biogenic ROG, the geographical variation in NO_x-ROG chemistry as an air mass ages and moves downwind from an urban center, and the influence of meteorological stagnation in causing day-to-day variations in NO_x-ROG chemistry. An understanding of these factors can be of great help to researchers and to regulators who need to interpret the results of models or other NO_x-ROG analyses.

The second part analyzes the specific chemical reactions and reaction sequences that create the division into NO_x-sensitive and ROG-sensitive regimes. This section also provides the theoretical basis for the link between NO_x-ROG sensitivity and the identified indicator ratios. O_3-NO_x-ROG chemistry is derived from reaction cycles involving odd hydrogen radicals (OH, HO_2 and RO_2, where R represents a carbon-hydrogen chain). NO_x-sensitive chemistry occurs when radical-radical reactions (HO_2+HO_2 and HO_2+RO_2, making peroxides) are the dominant sink for odd hydrogen, while ROG-sensitive chemistry occurs when nitrate-forming reactions ($OH+NO_2$, making nitric acid) are the dominant sink. From these chemical reaction sequences it is possible to derive a theoretical relationship between NO_x-ROG sensitivity and the species ratios that have been identified as photochemical indicators: O_3/NO_z and H_2O_2/HNO_3. Section 3 will show how the correlation between NO_x-

ROG sensitivity and photochemical indicators also appears in more complete photochemical simulations.

Results from Photochemical Simulations

Results for O_3-NO_x-ROG sensitivity from a series of photochemical simulations are presented and the correlation analyzed between NO_x-ROG sensitivity and the various photochemical indicators as predicted by the models.

Results are based on groups of three simulations: an initial scenario, a simulation with anthropogenic ROG emissions reduced by a fixed percentage (usually 35%) relative to the initial scenario, and a simulation with anthropogenic NO_x emissions reduced by the same percentage relative to the initial scenario. Results will be shown for a specific hour (usually in the afternoon, and corresponding to the time of peak O3 occurring in the initial model scenario). ROG-sensitivity will be reported as the difference between O_3 in the initial scenario and O3 in the simulation with reduced ROG at the same time and location. NO_x-sensitivity will be similarly reported as the difference between O_3 in the initial scenario and O_3 in the simulation with reduced NO_x. These results for model ROG- and NO_x-sensitivity will be presented in comparison with values for photochemical indicators at the same time and location in the initial model scenario. Results will typically be reported for every location in the model domain or sub-region of interest.

Complete graphical results will be shown for two indicator ratios: (O3/NOz) and (H_2O_2/HNO_3). Results for the other indicator ratios are visually very similar to these two, and will be presented in abbreviated form. In addition, a concise method for tabulating results of the NO_x-ROG-indicator correlation will be developed, based on a statistically defined transition between indicator values associated with ROG-sensitive chemistry and indicator values associated with NO_x-sensitive chemistry. This statistically defined transition point will be used to summarize results from all model scenarios and for each indicator ratio. Graphical results will also be shown for indicator ratios that did not correlate well with NO_x-ROG sensitivity: (O_3/NO_x) and the ratio of reactivity-weighted hydrocarbons to NO_y.

The simulation results shown here should not be interpreted as recommendations for specific ozone abatement strategies or as statements about NO_x-ROG sensitivity in specific locations. Many of the simulations use outdated inventories for anthropogenic emissions. Most of the simulations use the BEIS1 inventory for biogenics, which underestimates isoprene by a factor of three or more and consequently causes model results to be biased in favor of ROG controls. In addition, the selection of model scenarios for the NO_x-ROG analysis deliberately favored ROG-sensitive scenarios, especially for Atlanta. A meaningful evaluation of NO_x-ROG indicators is only possible in model scenarios that include both NO_x-sensitive and ROG-sensitive subregions, which did not occur in some of the NO_x-sensitive scenarios. Despite these caveats, the model NO_x-ROG results are offered as meaningful indications of NO_x-ROG sensitivity in relation to each other; i.e., the differences in NO_x-ROG sensitivity between model scenarios represent tendencies that are likely to be reproduced in other NO_x,-ROG models.

Results are based on five separate model applications: a regional-scale simulation for the Lake Michigan airshed, a regional-scale simulation for the northeast corridor, an urban-scale (UAM-IV) simulation for New York, an urban-scale (UAM-IV) simulation for Atlanta, and an urban-scale (UAM-IV) simulation for Los Angeles. Preliminary results are also shown for the Middle Tennessee Ozone Study in Nashville.

Results show the correlation between model NO_x-ROG sensitivity and (O3/NOz) for six model scenarios. The reduction in O_3 associated with a particular percentage reduction in anthropogenic ROG or NO_x emissions (usually 35%), defined as the difference between O_3 in the initial scenario and O_3 in the scenario with reduced ROG or NO_x at the same time and location. Negative values represent locations in which reduced anthropogenic emissions results in an increase in O_3. The simulated NO_x-ROG reductions are plotted for all locations in the model domain, in comparison with (O_3/NO_z) in the initial model scenario at the same time and location.

Each simulation shows a similar pattern. Locations with larger ozone reductions in response to reduced ROG rather than reduced NO_x (i.e., locations with ROG-sensitive chemistry) also have low (O_3/NO_z) (<8) in the initial simulation, while locations with larger ozone reductions in response to reduced NO_x (i.e., locations with NO_x-sensitive chemistry) also have high (O3/NOz) (>I0). There is also a well-defined value for (O_3/NO_z) that defines the transition between NO_x-sensitive and ROG-sensitive regions. This transition value remains the same in simulations for different metropolitan areas and for different model scenarios.

Results also show that the correlation between NO_x-ROG sensitivity and the indicator ratio (O3/NOz) remains consistent in model scenarios with very different overall NO_x-ROG results.

Summary and Conclusions

The report presents a series of results associated with the use of photochemical indicators as a basis for investigating O_3-NO_x-ROG sensitivity. The method of photochemical indicators seeks to identify species or species ratios that are closely associated with NO_x-ROG predictions in models. A successful correlation between model NO_x-ROG predictions and indicator values has been found for six species ratios: (O_3/NO_y), (O_3/NO_z), (O_3/HNO_3), (H_2O_2/HNO_3), (H_2O_2/NO_z), and (H_2O_2/NO_y). In each case, high values are associated with NO_x-sensitive model predictions for ozone and low values are associated with ROG-sensitive predictions. The close correlation between NO_x-ROG predictions and indicator values suggests that measured indicator values can be used as a basis for evaluating the accuracy of model NO_x-ROG predictions.

Indicator-NO_x-ROG correlations have been examined for a wide variety of model applications, including two different model types (UAM-IV and a regional model developed at the University of Michigan) with different photochemical mechanisms. They have been examined for several locations (Lake Michigan, northeast corridor, Atlanta and Los Angeles). They have been examined in model scenarios with a range of assumptions about emission rates, including scenarios with anthropogenic ROG emissions doubled or reduced by half in comparison with inventory values and scenarios with radically different emission rates for biogenic ROG. They have been examined in scenarios with changed wind speeds and vertical mixing heights. They have been examined in scenarios with strongly ROG-sensitive chemistry and in scenarios in strongly NO_x-sensitive chemistry. In all these cases, the correlation between model NO_x-ROG predictions and indicator values remains largely unchanged, even though the model NO_x-ROG predictions vary.

It is especially noteworthy that changes in model assumptions that affect NO_x-ROG predictions also cause a corresponding change in the model values for photochemical indicators. This feature is especially striking in the Atlanta case study. In this case, model predictions for O_3/NO_y concurrent with peak O_3 varied from 13 in the strongly NO_x-sensitive model scenarios to 6 in the ROG-sensitive scenario. The Atlanta case study is especially important because the NO_x-sensitive and ROG-sen-

sitive scenarios each give similar predictions for peak O_3, suggesting that an evaluation vs. measured O_3 does not provide a basis for confidence in model NO_x-ROG predictions. A similar contrast between NO_x-sensitive and ROG-sensitive scenarios is apparent in the scenarios for Lake Michigan with different ROG emission rates and in the simulations for New York /northeast corridor for events with different meteorology. The predicted contrast in indicator values between NO_x-sensitive and ROG-sensitive locations is partially confirmed by measurements in Atlanta and Los Angeles. Model results predict high values for O_3/NO_z in Atlanta and low values in Los Angeles. This prediction is consistent with measurements.

This study has identified a several factors that might be sources of error in the indicator method. A list of caveats is given in Section 1. The most important uncertainties are associated with the removal rate for the indicator species (especially through wet and dry deposition); the possible role of particulate nitrate as a sink for NO_y; and uncertainties associated with the chemistry of organic peroxides, which are not represented in some of the chemical mechanisms that are frequently used for air quality analysis (e.g. CB-IV). It is especially important to identify uncertainties that might lead to bias in the NO_x-ROG interpretation of indicator values.

A more general problem associated with the method of photochemical indicators is that, as with all methods designed to predict the sensitivity of O_3 to NO_x and ROG, it is very difficult to find direct confirmation that the predictions are accurate. This report has recommended investigation of model and measured correlations between O_3, NO_z and H_2O_2 as a basis for evaluating model assumptions that represent uncertainties in the indicator method. The models that were used to derive indicator-NO_x-ROG correlations also predict a linear correlation between O_3 and the sum: $NO_z+2H_2O_2$ This prediction should be verified vs. measurements. In addition, model results predict that the ratio $(O_3/O_z+2H_2O_2)$ should have similar values in NO_x-sensitive and ROG-sensitive locations (although it may show diurnal variations and day-to-day variation in responses to changing cloud cover and the effect of wet deposition). Because this ratio is closely associated with the proposed indicators (especially with O_3/NO_z), it might also be used as a basis for evaluating the accuracy of the proposed NO_x-ROG transition values associated with the indicators.

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The complete report, entitled "Evaluating the Relation Between Ozone, NO_x, and Hydrocarbons: the Method of Photochemical Indicators" (Order No. PB98-142 052; Cost: $36.00, subject to change) will be available only from:
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